SECONDARY STRUCTURE AND MOSAIC STRUCTURE OF CRYSTALS

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Abstract

In the following a brief summary is given of some of the essentials of the theory of the *secondary structure*. This structure is very sensitive to external disturbing effects which frequently cause the transition of crystals from thermally stable into *thermally pseudostable configurations* for which the term *mosaic structure* is proposed. A discussion of the relation of the mosaic structure to the secondary structure is given. The essentially new points of this paper are brought forth in §5, where it is shown that several very fundamental causes are operative during the growth of crystals which endanger the formation of thermally stable configurations. The most important of these causes is due to the fact that on solidification the heat of fusion must be carried away from the growing surface. The resulting temperature gradient very often is great enough to produce plastic deformations in the crystal in status nascendi. Finally a short review is given which intends to show that the adoption of the conception of a secondary structure and the closely related mosaic structure provides an adequate basis for the understanding of the totality of phenomena which is characteristic for the solid state of matter.

§1. Introduction

ONE of the most conspicuous phenomena very often exhibited by the solid state is a peculiar coexistence of perfection and imperfection in crystals. The purpose of this paper is to interpret the facts involved as being due to thermodynamically pseudostable states of crystal lattices. It will be assumed that crystals cannot satisfactorily be described by ideal lattices but that the introduction of a secondary structure is necessary. The reasons for the existence of a secondary structure have been discussed in previous publications.[1,2] In regard to the problem at hand I mention only that the existence of a sufficient number of thermodynamically pseudostable configurations of single crystals can hardly be understood from the standpoint of ideal crystallographic lattices. From the conception of a secondary structure, however, the possibility of pseudostable states may be derived at once and the coexistence of perfection and imperfection in crystals may be accounted for.

§2. On the Secondary Structure of Crystals

I have discussed in previous publications that different types of secondary structures are conceivable. For the following it will be sufficient to describe very briefly two special types A and B which possess all of the general characteristics which we require for our considerations.

[1] F. Zwicky, Proc. Nat. Acad. **17**, 524 (1931).
[2] F. Zwicky, Phys. Rev **38**, 1772 (1931).

A. Permanent electric polarization in crystals.

I have shown recently[2] why certain cubical heteropolar crystals have a tendency to change over into slightly tetragonal lattices which are characterized by permanent electric moments. It is not very hard to see under what circumstances this might happen. We must only apply the general laws of electrostatics to the electrostatic potential ϕ inside of an ionic lattice. Indeed, observing the equation

$$\Delta\phi = 0 \tag{1}$$

we must require that ϕ have neither real maxima nor minima throughout the lattice. Every extreme value of ϕ must be of the mixed kind (law of Earnshaw). If an ion is in a dynamically stable position with respect to a definite displacement there certainly will be another displacement with respect to which the position of the ion is unstable. A cubical lattice, for instance, if alternately occupied by positive and negative charges will be unstable with respect to a displacement of the negative and the positive lattice relative to each other. We denote this displacement with D_R where the index R indicates that this variation is closely related to the phenomenon of the infrared residual rays. A lattice which is built up of static charges is of course also unstable with respect to a compression D_C inasmuch as it has a tendency to contract as long as the mutual distances between the point charges are not zero. In order to account for the stability of crystals, M. Born therefore introduced the so-called repulsive forces between the ions. These forces were recognized by the wave mechanics as being due to the overlapping of the Schrödinger space charges of the ions. For a first pheno menological approximation it is sufficient to write for the mutual "repulsive" energy ϵ_{ik}^{+} of two ions i and k one of the following two expressions

$$\epsilon_{ik}^{+} = A/r_{ik}^{p} \tag{2}$$

or

$$\epsilon_{ik}^{+} = Ae^{-\nu r_{ik}} \tag{3}$$

where r_{ik} is the mutual distance of the two ions. The coefficient A and the exponent p may either be calculated from the wave mechanics or they may be adjusted by the use of two observations. If $p>1$ there will always be a value of A which makes the lattice stable with respect to a variation D_C. This statement might not be simultaneously true for the variation D_R, and it is suggested by Earnshaw's law that the instability will occur especially for low values of p in (2). I have indeed been able to prove that only for $p>6$ the crystal will be dynamically stable with respect to D_R, if the lattice is of the NaCl type.[2] It is important to notice that similar conditions exist if we consider the CsCl type or the ZnS type of a heteropolar crystal instead. If

$$1 < p < p_{cr} \tag{4}$$

and the critical p_{cr} is definitely greater than one, we shall have stability

against D_c and instability against D_R.* For $p > p_{cr}$ the dynamic stability is secured both for D_c and D_R. However, as long as p satisfies the inequality (4) no cubic lattice will be formed in spite of the perfect central symmetry of the building stones. This result is of great importance inasmuch as it suggests at once the necessity of the existence of a certain secondary structure.

Indeed, if p satisfies (4) the displacement D_R is energetically self-perpetuating and the crystal will assume a tetragonal configuration plus a macroscopic electric moment. The polarization however cannot be homogeneous throughout because of the neutralizing effects of the surfaces. I have shown in another place that a secondary structure of the type pictured in Fig. 1 will come into existence. The electric polarization P is accompanied by a certain distortion due to the electrostriction. There will for instance be an extension along P and a contraction normal to P, which changes the ratio between the

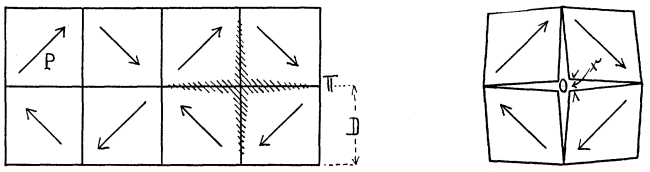

Fig. 1.

"longitudinal" and the "lateral" lattice constant by an amount Δ. The crystal therefore will have a tendency to assume the configuration A_M. For

$$D = d/\Delta \tag{5}$$

we shall have

$$x = d.$$

For approximately $D > d/\Delta$ the crystal would fall apart into separate blocks. This however will not happen because of two other effects setting in.

In the first place the electrostriction will be hindered by the mutual cohesion of the parts which are in contact along π. Stresses therefore will be set up in the shaded regions (Fig. 1).

In the second place a change of place of certain ions will occur. Indeed D will have a tendency to become as large as possible. This would increase the stresses in the point 0 so much that a rupture would occur and a hole be formed at 0. But if this hole becomes too large ions may be taken from the surface of the crystal and used for filling the hole.

The described type A of a secondary structure will possess the following

* In this connection the following phenomenon is of interest. It is known from the investigation of the respective band spectra, that for most metalhydride molecules $p < 6$, usually $3 < p < 4$. When the hydrides crystallize the hydrogen atom in the lattice is in a very unstable position. It vagabonds very easily or may be even expelled from the crystal. This is the case for instance for FeH which crystallizes with a partial expulsion of the hydrogen. I am indebted to Dr. O. Schmidt from Ludwigshafen for having called my attention to this peculiar behavior of the hydride on which our considerations may throw some light.

mechanical characteristics. If we denote an atom in an unstressed part of the crystal by the index p and an atom in the stressed part by π the respective potential energies ϵ satisfy this inequality.

$$\epsilon_p < \epsilon_\pi . \tag{6}$$

We denote with ϵ_I the energy of an atom in the corresponding ideal lattice which however possesses no electric polarization. Then Fig. 2 shows the relation between the different energies involved. ϵ_π may be greater or smaller than ϵ_I.

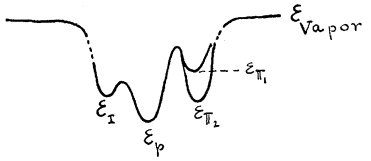

Fig. 2.

From (6) it follows that the rupture strength R against disrupting the crystal along π is less than the corresponding R_p.

$$R_\pi < R_p . \tag{7}$$

However, this conclusion may not be correct in every case as matters are complicated by the possibility of a greater density of atoms along π.

The resistance S against slipping will in general also be lowered.

$$S_\pi < S_p . \tag{8}$$

The inequality (6) indicates that it is easier to remove an atom from a π-plane than from a p-plane. Etching or evaporation would in this particular case attack the π-planes first.

B. Type of a secondary structure which is due to the tendency of forming linear and plane crystals.

If we consider plane and linear equilibrium configurations we generally find that their potential energies per atom are almost as large as the energy of an atom in the corresponding three dimensional crystal. It may even be shown that the lines or planes may in certain cases represent states of lower energy than the three dimensional lattice. Due to their small mechanical strength these configurations will hardly ever occur in reality. If a crystal is formed we shall have to expect that certain lines and planes in the crystal will try to retain their own characteristic equilibrium configurations. We thus arrive at the picture of interpenetrating lattices whose elements are points, lines or planes respectively. In other words, we may speak of a point lattice (p) with a superposed secondary structure of contracted lines or planes π.

π-planes and p-planes will be out of phase with respect to each other. U. Dehlinger has shown[3] that such configurations may very well be dynamically

[3] U. Dehlinger, Ann. d. Physik **2**, 786 (1929).

stable. Dr. H. M. Evjen[4] and the author have given examples of such configurations which represent lower energy states than the usual ideal crystallographic arrangements. This is due mainly to the polarizability of the atoms of which proper use is made only in slightly asymmetrical arrangements.

The secondary structure of the type B possesses the following mechanical characteristics. In this case

$$\epsilon_p > \epsilon_\pi \tag{9}$$

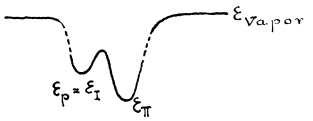

Fig. 3.

which is just the reverse of what holds true for the type A. Fig. 3 contains the relation between the different energies involved. From this it follows that the relation (7) is also reversed.

$$R_\pi > R_p \tag{10}$$

whereas the inequality (8) holds true for the type B as well.

$$S_\pi < S_p. \tag{11}$$

This is due to the fact that planes in the neighborhood of π are out of phase with respect to each other. We may compare a π-plane to an almost liquid layer whose cohesion, R, is large but whose resistance against slipping is very small.

§3. On the Mosaic Structure of Crystals

From the discussion in the previous section it must be concluded that the secondary structure is considerably more sensitive to external disturbances than the primary structure. Structure sensitive properties therefore have their origin mainly in the secondary structure.

The previous considerations also suggest that we attribute imperfections of crystals to distorted configurations of the S.S., at least as long as these imperfections are not too great. It can easily be shown that such distorted configurations of the S.S. may be dynamically stable and therefore thermodynamically pseudostable. Distorted configurations of the S.S. must be expected to be very frequent as will be shown later on. In spite of being quite inconspicuous, geometrically speaking, they nevertheless influence the physics of a crystal enormously. For this reason it seems advisable to introduce a terminology which will enable us to distinguish between thermally stable and pseudostable configurations of crystal lattices. I propose to use the terms *Secondary Structure* (S.S.) and *Mosaic Structure* (M.S.) respectively. Unfortunately, I have used in my previous publications those two terms indiscriminately. This really was not justified because of the regularity of the S.S.

[4] H. M. Evjen, Phys. Rev. **34**, 1385 (1929).

which has no mosaic aspect. The new proposal seems logical for the following reasons. It at the same time correlates and distinguishes between *perfections* and *imperfections* in real crystals. The above distinction is also in agreement with the old usuage of the word mosaic structure by Darwin, Ewald and others. It furthermore suggests an intimate relation between the thermally stable and pseudostable states of crystals.

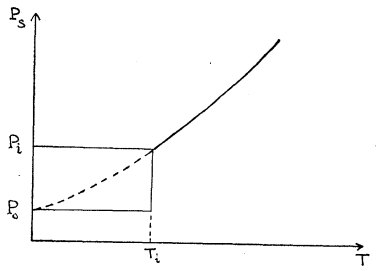

Fig. 4.

In order to illustrate the previous remarks it will be advantageous to point out briefly a few of the possible types of mosaic structures.

In the first place it is quite possible that in a real crystal by some reason or other the π-planes of the S.S. are not equally spaced. In other words the blocks characterizing the S.S. may not all be of the same size. If such a configuration is dynamically stable a certain thermal agitation is needed in order

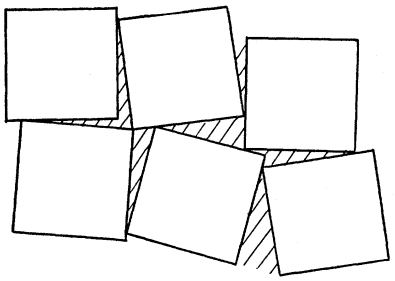

Fig. 5.

to throw the crystal from the above pseudostable configuration into a thermally stable state. We might call the temperature which is required the *ignition temperature* T_i of the S.S. crystals in solution may for instance be formed at a temperature $T < T_i$ and exhibit different properties from crystals grown out of the melt.

It is important to notice that the existence of an ignition temperature accounts readily for hysteresis effects in single crystals. We shall indeed expect for any structure sensitive property P_s of the crystal a dependency on the temperature as shown in Fig. 4. Only for $T > T_i$ will P_s be a univalued function of T. For $T < T_i$ it may for given T assume any value between P_0 and P_i depending on the previous history of the sample.

Hysteresis effects in single crystals are well-known. The theory of the ideal crystal lattices so far has not been able to account for phenomena of this type.

A second type of thermally pseudostable configurations may be arrived at if a plastic deformation of a single crystal is introduced. According to §2 slips will occur preferably along certain π-planes. This will lead to configurations as shown in Fig. 5. Deformations have taken place along the shaded regions only. The inside of the blocks, due to their high shearing strength along the p-planes will essentially stay intact. This is in excellent agreement with the observed Laue patterns of deformed crystals.

It is interesting that the conception of the secondary structure also provides a qualitative understanding of the *cold hardening* of single crystals, which phenomenon constitutes an unsurmountable difficulty for the theory of the ideal lattices. Indeed if we are dealing with a S.S. of the type B, we have

$$S_p > S_\pi \quad R_\pi > R_p.$$

In a typical case (rock salt) we would for instance have approximately

$$S_\pi = 10\,\mathrm{kg/cm^2} \quad R_p = 20{,}000\,\mathrm{kg/cm^2}.$$

S_π is the observed value. R_p is calculated under the assumption of an ideal lattice.[5] If we strain our crystal, a plastic deformation in the form of a series of slips will set in due to the low value of S_π. From Fig. 5 it appears that after a certain deformation pure slipping is impossible due to the slight turning of the blocks. In order to increase the deformation one must pull the blocks apart. The resistance against rupture is determined by the much higher value R_p. In this way it may be possible to arrive at an understanding of the cold hardening of single crystals.

In order to effect the transition from the configuration (5) back to the perfect crystal a certain thermal agitation is necessary. Configuration (5) therefore also represents a thermally pseudostable configuration.

In the third place we must consider the influence of impurites. The free energies of two identical foreign atoms in a π-plane and in a p-plane respectively will be different. The equilibrium concentration of the foreign atoms in the two types of planes will therefore be different. If the foreign atom does not fit into the ideal lattice we may expect it to favor the π-plane. We thus arrive at the picture of enantiomorphic atoms being imbedded in the crystal structure in the form of layers. If the distribution of the foreign atoms in the π-plane is not uniform we again may expect pseudostable configurations, at least for $T < T_{cr}$ where T_{cr} is the temperature at which effective migration of the foreign atoms begins to take place.

Only the second of the above cases (Fig. 5) leads to a design which ordinarily is associated with the word mosaic. We however generalize this conception and propose to call *every thermally pseudostable configuration of a lattice a mosaic structure.*

[5] F. Zwicky, Phys. Zeits. **24,** 131 (1923).

Finally it is of interest in this connection to mention a peculiar consequence of the conception of the secondary structure.

If we are dealing with an infinite crystal, the secondary structure relative to a given point in the lattice may be shifted around. There is nothing to fix the position of the S.S. relative to a given point in the primary lattice. As soon as we deal with crystals of finite size however, the S.S. will be anchored in a definite position because of the action of the surfaces of the crystal. Vice versa, the S.S. must have some effect on the formation of the surfaces. Due to the existence of the S.S. which is suspended between the surfaces of the crystal like a spider webb in an enclosure, we must expect that the different surfaces influence each other. This interaction will depend on the volume of the crystal. There are of course other volume effects which are due to the ordinary surface tension. Let us consider which quantity is important for the difference in vapor pressure of finite crystals or of finite drops due to the surface tension. The following quantity Γ_σ may be shown to be characteristic

$$\Gamma_\sigma = \frac{3\delta\epsilon_\sigma}{r} \Big/ \frac{3kT}{2} \tag{12}$$

because

$$\ln p'/p = \frac{2\delta\epsilon_\sigma}{rkT} \tag{13}$$

where p and p' are the respective pressures of an infinite and a finite volume and where δ and r are of the linear dimensions of an atom and the drop or crystal respectively, and ϵ_σ is the surface energy per atom.

If we take into account the S.S., we find that similar volume effects must be expected which under certain circumstances may be far more important than those caused by the ordinary surface tension. Indeed the layer of atoms which we introduced in the previous considerations must now be replaced by a layer of blocks of the linear dimension D, inasmuch as the surface blocks may be characterized by an energy difference $\epsilon_p' - \epsilon_\pi'$ per atom which may be considerably different from the corresponding quantity $\epsilon_p - \epsilon_\pi$ characterizing the inside of a block. The difference

$$\epsilon_S = (\epsilon_p - \epsilon_\pi) - (\epsilon_p' - \epsilon_\pi') \tag{14}$$

may very well be of the same order as ϵ_σ, namely, approximately 10^{-14} ergs, as follows for instance from my calculations on the S.S. caused by the existence of self perpetuating electric moments.[2] The characteristic quantity now therefore is

$$\Gamma_S = \frac{3D\epsilon_S}{R} \Big/ \frac{3kT}{2} \cdot \tag{15}$$

The S.S. then for a linear size of approximately

$$R = rD/\delta \tag{16}$$

of the crystal grain causes pressure effects similar to those which the ordinary surface tension σ produces for crystals of the dimension r. Now if

$$D/\delta = 10^4 \tag{17}$$

which according to my previous calculations is very well possible, we must expect volume effects due to the S.S. for $R=1$ mm which are comparable to those produced by the ordinary surface tension for $r=10^{-5}$ cm. This may be the explanation for the well-known fact that the individual grains in a polycrystalline aggregate behave similarly to a bunch of soap bubbles in contact with each other. The membrane between a small and a large bubble is always convex with respect to the outer normal of the small bubble, see Fig. 6. (I am indebted to Dr. I. Langmuir for having called my attention to this phenomenon and having suggested a possible relation to the S.S.) Arrangements similar to that shown in Fig. 6 are found on many polished and etched surfaces of polycrystalline metals. It is also known that many salts crystallizing out of solution exhibit small crystals "growing" into the bigger ones.

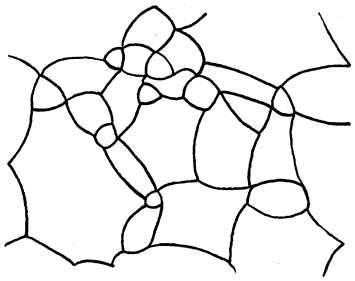

Fig. 6.

§4. On a Paradox Concerning the Free Energy of Real Crystals

We know from experience that thermally stable configurations are not always realized in nature. There are two reasons for this.

In the first place the reaction which is required for the transition to the stable state to take place may be dynamically impossible at least at low temperatures. For instance H_2 and O_2 will in general not be in equilibrium at room temperature as the reaction rate into H_2O is too small. However, we do not know anything about the dynamical aspects of the formation of crystals and we shall not therefore dwell on this question any further. For the following it is of importance only that thermally pseudostable states of crystals exist.

In the second place there are continually acting external disturbances, which under certain circumstances may cause the reverse transition from the thermally stable states to unstable states. Several types of such disturbances will be discussed in the next section. From the considerations there given it will become clear that *a great number, if not most of the crystals which have been formed naturally are in thermally pseudostable configurations.* They therefore fall into the category of crystals with a *mosaic* structure. Real crystals

thus most frequently exhibit a mosaic structure. They will show a S.S. proper only under very special circumstances.

The paradox which I wanted to mention in this connection is the following.

Suppose that the formation of an ideal crystal were really possible. Its mechanical strength then should be hundreds of times greater than the strength of most pure real crystals. This great mechanical strength would be sufficient protection against most of the accidental disturbances or fluctuations in nature to safeguard the existence of ideal crystals.

From previous considerations it is probable that ideal lattices, if at all possible, can be formed only under very particular circumstances, namely, if the symmetry character of the primary and the secondary structure is the same. Real crystals on the other hand will in general be so weak that the omnipresent disturbances in nature very often endanger the thermally stable configurations (ϵ_π) and cause the crystals to go into pseudostable configurations (ϵ_M). This will be discussed in more detail in the next section. We therefore will be very often confronted with the following paradoxial situation.

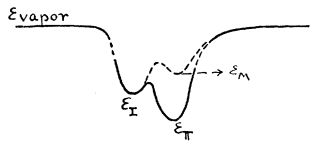

Fig. 7.

Crystals, for reasons developed elsewhere,[1] favor lattices characterized by secondary structures. The existence of these S.S. implies an excessive weakness of the crystals with regard to slipping. The crystals therefore are easily plastically deformed and are thrown into mosaic configurations (ϵ_M). It may then happen that $|\epsilon_M|$ is not only smaller than $|\epsilon_\pi|$ but also

$$|\epsilon_M| < |\epsilon_I| . \tag{18}$$

so that the resulting *real crystal is thermally even less stable than the ideal crystal* if the latter could exist. This suggests as a quantitative energetic criterion of a *single crystal* the requirement

$$|\epsilon_M| > |\epsilon_I| . \tag{19}$$

If we are dealing with a secondary structure of the type B it is quite possible to decide between (18) and (19) experimentally. Case (18) will produce grooves on evaporation and etching whose starting points must lie on the π-planes. In case (19) on the other hand the grooves will start in the center of the ideal blocks. These conditions have been verified by Dr. Goetz[6] and myself[7] in the case of single crystals of Bi and Cu. The experiments involved also dispose of the trivial objection that the patterns which we have observed on the Bi-single crystals are due to slip lines on an otherwise ideal lattice.

[6] A. Goetz, Proc. Nat. Acad. **16,** 99 (1930).

[7] F. Zwicky, Proc. Nat. Acad. **15,** 816 (1929).

§5. On Some Causes for the Formation of Mosaic Structures

With the formation of crystals there are necessarily related some fundamental phenomena whose presence often causes the crystals to go into mosaic configurations. The present paragraph is devoted to a discussion of some of these effects.

A. The heat of fusion as a cause of plastic deformation.

On the solidification of G grams of solid out of the melt an amount of heat $G \times H$ is liberated, where H is the heat of fusion per gram. This heat must be carried away which necessitates the existence of a temperature gradient. The temperature in the crystal is highest at the growing surface. This surface therefore plays the role of a generator of heat in motion. The temperature gradient in turn creates thermal stresses which may, if great enough, deform the crystals in *status nascendi*.

The determination of the resulting stresses involves the solution of the following problem. Given are the heat conductivites and the heat capacities of the crystal and the surrounding media, melt, walls of the container, etc. The initial distribution of temperature and the speed of growth of the crystals are supposed to be known, from observation for instance. What will then be the distribution of temperature at a subsequent time t? The solution of this problem will evidently be obtained as a solution of the general differential equation for the heat conduction, taking into account the generation of heat on the growing crystal surfaces.

Exact solutions of the problem stated for some simple cases will be given in another place. For the present discussion it is sufficient to give an estimate of the stresses which must be expected. For this purpose we may proceed as follows. Suppose that our crystal grows in the form of a rod of constant cross-section q at a speed of v cm/sec. In order to get the order of magnitude of the temperature gradient at the growing surface, we assume that the whole amount of heat generated is carried away through the crystal, whose heat conductivity may be denoted with λ. The temperature gradient dT/dX will then be

$$\lambda \frac{dT}{dx} = \rho v H. \tag{20}$$

Here X is measured along the rod, ρ is the density of the crystal and H the heat of fusion per unit mass. The gradient dT/dX if distributed over a length L, causes a maximum angular distortion γ of approximately

$$\gamma = \alpha \frac{dT}{dx} L \tag{21}$$

where α is the linear coefficient of expansion. This strain corresponds to a stress σ whose order of magnitude is given by

$$\sigma = \tau\alpha \frac{\rho v H}{\lambda} L \tag{22}$$

where τ denotes the shearing modulus. If we insert actual values for the different parameters we obtain stresses which are considerable and which may distort the crystal in its state of growth.

For instance for NaCl we have $\tau = 1.29 \times 10^5$ kg/cm^2, $H = 123.5$ cal. gr, $\alpha = 1.06 \times 10^{-4}$ between 25° and 50° centigrade, $\rho = 2.17$, $\lambda = 0.0116$ cal./cm sec. degree at 100°C. The value of λ will be smaller at the melting point as it is decreasing with increasing T. We therefore obtain approximately

$$\sigma = 3 \times 10^5 v \times L \text{ kg/cm}^2. \tag{23}$$

For $v = 10^{-3}$ cm/sec. and $L = 10^{-2}$ cm this results in

$$\sigma = 3 \text{ kg/cm}^2. \tag{24}$$

The shearing strength of NaCl is of the order of 10 kg/cm^2 at room temperature and decreases considerably with increasing T. It follows then that under the above circumstances we must expect an intrinsic plastic deformation of rock salt crystals during their growth out of the melt. This plastic deformation may in certain cases be removable by annealing the crystals at high temperatures. In general the crystal will remain in a slightly deformed state until it cools to temperatures at which the deformed states represents a thermally pseudostable configuration.

For the artificial methods of growth in general the same considerations hold true. Crystals of the alkali-halides obtained by the Kyropoulos method usually are grown with speeds of one or more cm an hour which gives stresses of the same order of magnitude as computed above.

For metals similar results are obtained. In the case of Bi for instance we have $H = 10 - 12$ cal./gr, $\rho = 9.8$, $\alpha = 1.29 \times 10^{-5}$, $\lambda = 0.017$ cal./cm sec. degree at 200°C, $\tau = 9.7 \times 10^4$ kg/cm^2. This results in

$$\sigma = 7.34 \times 10^3 v L.$$

For some of the most carefully grown Bi single crystals $v = 10^{-2}$ cm/sec., $L = 0.1$ cm. Therefore

$$\sigma = 7.34 \text{ kg/cm}^2.$$

The shearing strength at room temperature is of the order of 20 kg/cm^2 and 10 kg/cm^2 at 500°.

The relation (22) allows us to draw a few very interesting conclusions. It is seen that σ is depending on the length L over which the temperature gradient prevails. This suggests an explanation for the frequently observed phenomenon that crystals during their natural growth attain only a certain size. According to the above considerations this may be due to the fact that the plastic deformation prevents further growth as soon as L surpasses a certain critical value.

It is also possible that the differential equation of heat conduction which governs the problem stated in the above admits of periodic solutions in time. Physically speaking this would mean, that as the speed v increases, the temperature near the growing surface increases due to the impossibility of carry-

ing off the heat fast enough. The increasing temperature in turn slows down the growth of the crystal and the whole process repeats itself. This possibility may have some bearing on the macroscopic periodicities observed by Straumanis[8] during the artificial growth of Zn crystals.

B. Other causes for the plastic deformation of crystals

There are still some other causes, which prevent the formation of perfect crystals. One of them is related to the fact that the melt and the crystal have different solubilities for gases. It happens for instance that the melt may contain an amount of gas ten or more times greater than the solid. The greatest part of the dissolved gas then must be liberated on solidification. This process if it assumes violent forms is known as spitting or spurting. Craters may be formed on the growing surface or pockets inside the crystal which evidently destroy the perfection of the crystals grown under such conditions.

In rare cases gravity may be active in disturbing the formation of good crystals. This effect can play a role if heavy crystals are formed whose shearing strength near the melting point is very small.

The earth's magnetic field might also have some influence. It would be interesting for instance to grow crystals of very pure iron in the earth's magnetic field and in field free space.

C. Methods to prevent the disturbing effects during the growth of crystals

From the above it follows immediately that it is possible to avoid the causes of intrinsic plastic deformation discussed in the section A and B.

The difficulty related to the transport of the heat of fusion is evidently best avoided if v is made small artificially and if one grows the crystals at low temperature, which is advantageous because of the increase of shearing strength with decreasing T. Low speeds of growth applied to crystals formed from the melt, however, do not always help because of the supercooling effects introducing other disturbances. The slow growth of crystals out of solution or out of the vapor therefore seems to offer the best guarantee against the disturbance discussed under A. The growth out of the solution however is not always possible. In addition there are other peculiar difficulties related to it, such as effects of impurities, differences in the concentration of the solution and the convection currents set up during the crystallization, etc. There remains the precipitation of crystals from the vapor in vacuum. Very good crystals have indeed been obtained already by this method.

Of the other difficulties mentioned under B, all of them can be avoided by observing proper precautions during the artificial growth except those due to the influence of gravity.

The main purpose of this paragraph was to show why naturally grown crystals are seldom perfect and that great precaution is necessary if one wishes to distinguish between thermally stable and pseudostable states.

[8] M. Straumanis, Zeits. f. anorg. Chemie. **181,** 1 (1929).

§6. Concluding Remarks

In the preceding section I have tried to show that there are a number of very fundamental effects active which endanger the realization of thermally absolutely stable configurations of crystals. These effects are of such an intrinsic nature that one might conclude that they never can be completely avoided. One might further conclude that one could account in this way for all the peculiar difficulties which the theory of *ideal crystal lattices* has encountered so far without any apparent means of disposing of them. I think this would be a mistake. Different investigators including the present writer have thoroughly discussed this possibility in the near past and shown that any attempt to account for the failure of the theory of ideal lattices in this way is quite futile. The solution of the problem of the solid state must be of a more fundamental nature. Some radical modification of the theory, such as I have proposed, with the conception of a secondary structure, I think, is unavoidable. It may be good to recall here briefly once more a few of the peculiar characteristics of the solid state for which the theory of ideal lattices has proved incapable of providing any solution.

(1) The mechanical strength is hundreds to thousands of times smaller than might be expected from the theory of ideal lattices. The break-down occurs within the region of strict validity of Hooke's law, this in spite of the fact that the second order terms in the expansion of the forces are undoubtedly present and not negligible at all. This latter fact must be inferred from the existence of a thermal coefficient of expansion, which is different from zero.

The effect of cold hardening of single crystals means that the crystal lattice becomes stronger after it has been actually destroyed.

(2) Incomprehensible for the theory of ideal lattices is also the peculiarly low solubility of certain impurities in the crystal lattice. The fact cannot be explained in the same way as the low solubility in liquids which is due to fast recombination of the dissolved particles.

The enormous influence of very small amounts of impurities on structure sensitive properties also presents a hard problem.

(3) The sharpness of the melting points and the absence of an increase of the specific heat below the melting point suggest that certain cooperative effects between many atoms must be responsible for the existence of crystals. This view is consistent with the occurence of volume effects as mentioned in §3. It also accounts for the crystal growth through old grain boundaries made up of impurities. Generally speaking, cooperative effects are necessary for the understanding of the peculiar coexistence of perfection and imperfection in single crystals.

(4) The above difficulties have led the author to the conception of a secondary structure. Many new effects could be derived and predicted from this conception. The experimental verifications which have been obtained naturally present new problems if one does not accept the views from which they have been inferred.

Beside the investigations carried out in this Institute the recent researches of Straumanis[9] and Bitter are particularly significant.

Straumanis grew single crystals of Cd and Zn out of the vapor and obtained secondary structures such as we have observed first on Bi in this Institute. This is of great bearing as we have shown that this method of growth of crystals is particularly adapted for avoiding accidental imperfections.

Finally F. Bitter's[10] recent beautiful experiments on the existence of a magnetic secondary structure of ferromagnetic crystal when put in a magnetic field are of utmost importance. This because of the fact that this secondary structure may be shifted at will by switching off the magnetic field and putting it on again.

The above arguments I think suffice to justify the adoption of the theory of the secondary structure as a reasonable working hypothesis. The purpose of this paper was to show that this theory combined with corresponding considerations on the closely related mosaic structure provides a framework which seems well adapted for the systematic investigation of the physics of the solid state.

[9] M. Straumanis, Zeits. f. physik. Chemie **13,** 316 (1931).
[10] F. Bitter, Phys. Rev. **38,** 1903 (1931).